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Polarized Infrared Spectra of Planar Molecules*

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A new method was proposed for the determination of the direction of the transition moment associated with a given molecular vibration, and was shown to be applicable to orthorhombic crystals consisting of molecules with a C_s , C_{2h} or C_2 symmetry. The direction of the transition moments of succinimide were estimated by this method and compared with those expected from Uno and Machida's assignments. A good agreement was obtained between the present determination and their assignments. However, one of bands which was found to be corresponding to the CH_2 rocking vibration by this method had been assigned by these authors to the skeletal vibration and vice versa.

The method was also applied to molecules with two C_s symmetry groups, like acetanilide. Here, the absorption bands were found to be classified into those associated with vibration of benzene ring and those with amide group. Each set of the band was subdivided into those associated with the in-plane and out-of-plane vibrations. The absorption bands were assigned in accordance with the directions of the transition moments. It was also found that the influence of the molecular interaction on infrared active vibrations was negligible in the case of succinimide and acetanilide.

INTRODUCTION

The determination of the direction of the transition moment associated with a given molecular vibration is useful for the assignment of the band, presumption of the crystal structure, and calculation of the absorption intensity. So far, not so many applications¹⁻³⁾ have been made to actual molecules because of experimental difficulties. Further, it has not been established yet whether molecular interaction in crystal was considered to be negligible. In the previous paper⁴⁾, directions of transition moments of hydrogen out-of-plane vibrations and their combination bands were calculated from dichroic ratios. It was concluded that the interaction between molecules within the unit cell was negligible concerning these vibrations. In this paper, the influence of the molecular interaction on infrared active vibrations of succinimide and acetanilide will be discussed.

The ordinary method⁵⁾ for calculating the direction of the transition moment requires time-consuming procedures and is tedious to exclude the ambiguity⁴⁾ arising from the crystal symmetry. The method presented in this paper improves these points for the determination of the direction of the transition moment

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associated with a given molecular vibration. It can generally be used for orthorhombic crystals consisting of molecules* with the C_s symmetry. The infrared spectra of succinimide⁸⁻¹⁰⁾ have been reported in many papers. Uno and Machida¹⁰⁾ have investigated the spectral change on deuteration of succinimide and maleimide, and have given assignments to the imide group. Their assignments will be discussed in this paper by referring to the directions of transition moments.

The present method is further applied to molecules with two C_s symmetry groups. Thus, the absorption bands can be classified into the two sets of bands associated with each group, which is subdivided into the in-plane and out-of-plane vibrations. Brown and Carbridge¹¹⁾ have made X-ray analysis of acetanilide and found that both the amide group and benzene ring have approximate symmetry planes, and the angle between the two planes is about 30° . Abbott and Elliott²⁾ have measured the polarized infrared spectra of oriented crystals of acetanilide and deuterated compounds and have given the directions of the transition moments. Thus the assignment of acetanilide is reexamined by the present method and the product rule.

THEORY

If, in the case of orthorhombic crystals, D_j , D_k and D_l are optical densities with the E vector along j , k and l crystal axes respectively, the angle (θ_k^l) between the k axis and the projection of transition moment to jk plane can be

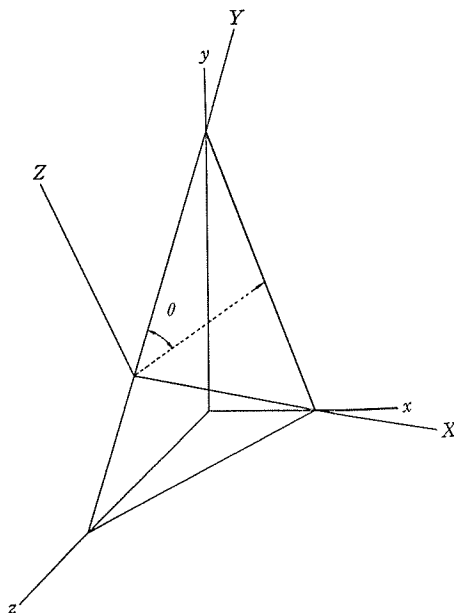


Fig. 1. Crystal axes and the new coordinates.

* In the present paper, the method is discussed only for the molecules with the C_s symmetry. It can, however, be applied for molecules with the C_{2h} or C_2 symmetry. In the case of C_2 symmetry, the plane perpendicular to a fold axis should be considered for the calculation, instead of the symmetry plane.

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Table 1. Atomic coordinates of succinimide (A unit).

atom	X	Y	Z
N ₁	-0.523	-1.647	-0.057
O ₁	-2.541	-2.766	0.011
O ₂	1.709	-1.082	-0.008
C ₁	-1.298	-2.777	-0.017
C ₂	0.845	-1.930	-0.002
C ₃	-0.392	-3.990	0.033
C ₄	0.843	-3.420	-0.003
H ₁	-0.93	-0.81	0.15
H ₂	-0.43	-4.76	-0.83
H ₃	-0.54	-4.52	0.66
H ₄	1.57	-3.89	0.80
H ₅	1.63	-3.86	-0.86

expressed as follows :

$$\theta_k^j = \tan^{-1} \left(-\frac{D_j}{D_k} \right)^{1/2} = \tan^{-1} (D_k^j)^{1/2} \quad (1)$$

This relation can be used only when the coupling between the molecules within the unit cell is small and no accidental degeneracy exists.

The vibrations of C_s molecules are divided into the in-plane and out-of-plane vibrations, which have directions of transition moments perpendicular and parallel to the symmetry plane respectively.

In the case of succinimide, Mason¹²⁾ has reported that the equation of the plane containing the carbon, nitrogen and oxygen is evaluated to be

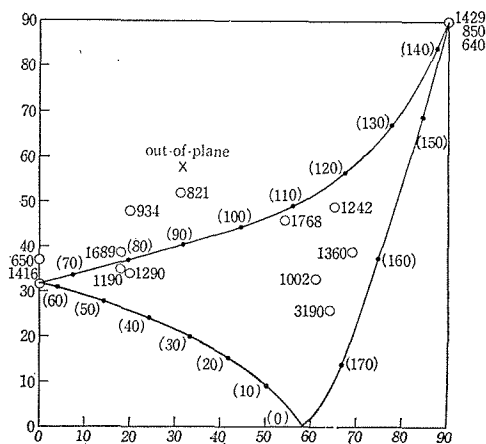
$$0.8096x + 0.3090y - 0.4991z + 0.1142 = 0 \quad (2)$$

and the atomic deviation from this plane are very small. Here x , y and z are coordinates (in Å unit) corresponding to a , b and c crystal axes respectively.

The new axial systems are defined as shown in Fig. 1, where XY plane is identical with the plane expressed in equation (2) and the Z axis is normal to the plane. Table 1 shows the atomic coordinates of succinimide in terms of the new coordinate system and Fig. 4 shows the projection of the molecule to XY plane.

The $\theta_c^x[X]$ and $\theta_c^y[X]$ are the angles formed by the c crystal axis against the projections of the transition moment to the ac and bc planes respectively. For the in-plane vibration, $\theta_Y^X[X]$ is the angle between the Y axis and the direction of the transition moment (the direction of the arrow in Fig. 1). When the $\theta_Y^X[X]$ is varied in the range $0^\circ \sim 180^\circ$ and $\theta_c^x[X]$ and $\theta_c^y[X]$ are calculated and plotted to ordinate and abscissa respectively, a closed curve is obtained as shown in Fig. 2, where the numbers in parenthesis are values of $\theta_Y^X[X]$ at intervals of ten degrees. On the other hand, $\theta_c^x[X]$ and $\theta_c^y[X]$ of the transition moment of the out-of-plane vibration, which is normal to the plane of equation (2), are obtained and shown by a mark X in Fig. 2.

This method may be applied to molecules with two C_s symmetry groups,


 Fig. 2. θ_e^a - θ_e^b plotting of succinimide.

provided that the vibration of each group do not couple each other.

Acetanilide molecule consists of the amide group and benzoic group, each of which having an approximate symmetry plane which is evaluated to be

$$x - 0.771y - 2.278z = 5.514 \quad (3a)$$

and

$$x - 2.658y - 3.897z = 2.086 \quad (3b)$$

respectively.

In the same manner as succinimide, atomic coordinates of the amide and benzoic groups of acetanilide were expressed in terms of new coordinate systems as shown in Tables 4 and 5 respectively. The projection of the amide group to XY (A) was shown in Fig. 8, and that of benzoic group to XY (B) in Fig. 9.

EXPERIMENTAL

The sample used were obtained from the Tokyo Kasei Co., and were further purified by recrystallization. Well oriented crystal layers of these samples were obtained by cooling the melts between two optically flat plates of rock-salt. Fairly large areas of uniform orientation were produced by touching the melted samples at the edge of one of the windows with the seed crystals. In this case, the oriented crystals in which various crystal planes are parallel to the surface of rock-salt were obtained. Then, the Miller indices of the planes were determined by using a Shimadzu GX-2A X-ray diffractometer. Infrared spectra were measured by using a Koken DS-301 spectrometer equipped with two NaCl prisms.

RESULTS AND DISCUSSION

1. Succinimide

Figures 3(a) and (b) show that the polarized infrared spectra of two kinds of samples, in which (100) and (010) crystal faces are parallel to the surface of

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rock-salt respectively. Dotted, broken and full lines are the absorption curves obtained with the polarized radiation having the E vector parallel to the a , b and c crystal axes respectively. Dichroic ratios were corrected for imperfection of polarization in the transmitted beam of AgCl polarizer⁴). Table 2 shows these values, together with θ_c^a and θ_c^b obtained by using equation (1). When θ_c^a and

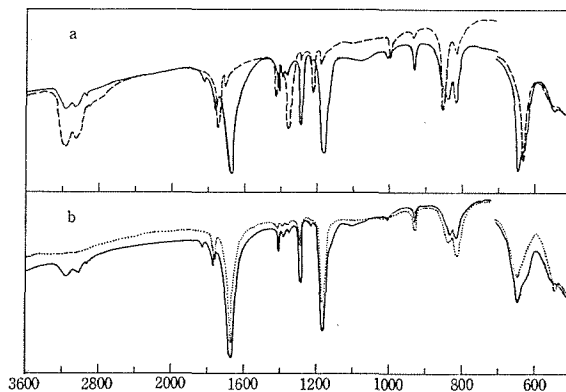


Fig. 3. Polarized infrared spectra of succinimide.

a : 100 section. b : 010 section.

— E vector along a axis.

----- E vector along b axis.

..... E vector along c axis.

Table 2. Frequencies, dichroic ratios, directions of transition moments and assignments.

Frequencies (cm ⁻¹)			D_c^b	θ_c^b	D_c^a	θ_c^a	θ_Y^x	Assignments
a	b	c						
3190	3190	3190	4.39	64°	0.23	26°	166°	NH st.
3080	3080	3080	3.12	61°	0.19	24°	168°	Combination
2960	2960	2960						CH st.
1768	1768	1780	1.85	54°	1.02	46°	108°	C=O st.
1689	1722	1689	0.08	18°	0.64	39°	80°	C=O (\cdots H) st.
—	1429	—	∞	$\sim 90^\circ$			$\sim 145^\circ$	CH ₂ sym. bend.
1416	—	1416	0	0°	0.37	31°	63°	NH bend.+CNC st.
1397	1402	1397	<1	<45°	0.75	41°	$\sim 90^\circ$	CH ₂ asym. bend.
1360	1372	1370	6.69	69°	0.67	39°	160°	CNC sym. st.
1290	1290	1295	0.14	20°	0.68	34°	80°	CH ₂ wagg.
1242	1240	1242	4.71	65°	1.36	49°	115°	CH ₂ twist?
1190	1199	1190	0.10	18°	0.50	35°	79°	NH bend.+CNC st.
1002	1001	1005	3.33	61°	0.43	33°	163°	Skeletal
934	935	936	0.13	20°	1.25	48°	86°	Skeletal
—	850	—	∞	$\sim 90^\circ$			$\sim 145^\circ$	Skeletal
841	—	841	<1	<45°	1.79	53°		NH out-of-plane bend.
821	823	820	0.36	31°	1.68	52°		CH ₂ rocking
650	—	650	0	0°	0.56	37°	65°	C=O asym. bend.
—	640	—	∞	$\sim 90^\circ$			$\sim 145^\circ$	C=O sym. bend.
558	558	558	<1	<45°	>1	<45°		C=O out-of-plane bend.

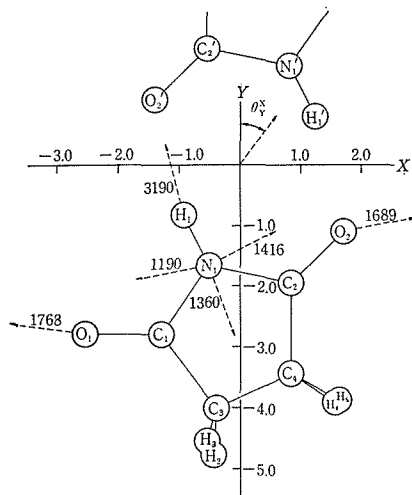


Fig. 4. Projection of succinimide molecule to XY plane and directions of transition moments.

θ_c^0 are plotted in Fig. 2, a position corresponding to a band at 821 cm^{-1} are close to the position marked X, and these corresponding to the other bands are on or close to the curve. θ_Y^X are obtained from this figure. Fig. 4 shows several examples of θ_Y^X thus obtained.

1.1. Characteristic bands of the imide group. Characteristic bands of the imide group have been discussed in many papers, particularly on the spectral change in deuteration by Uno and Machida¹⁰⁾. Therefore, the directions of transition moments obtained by the present study were compared with their assignment.

A band at 3190 cm^{-1} has been assigned to the NH stretching vibration. The direction of the transition moment of the band is in agreement with the NH bond direction as shown in Fig. 4. On the other hand, the band is expected to have a parallel dichroism, because it is known from the X-ray analysis that the $\theta_c^0(X)$ and the $\theta_c^0(X)$ of NH bond are 54° and 86° respectively. But the spectra of the sample in which (010) crystal plane is parallel to the surface of rock-salt show the parallel dichroism. This indicates clearly that the accurate direction of the transition moment does not coincide with the NH bond direction. The θ_Y^X obtained from dichroic ratios is at an angle about 12° to the NH bond direction whose $\theta_Y^X(X)$ is 154° , but agrees with the direction of hydrogen bond ($\theta_c^0(X)$ is 59° , $\theta_c^0(X)$ is 33°). Similar results, in which NH band direction does not coincide with the direction of the transition moment, have been reported for some trans amide compounds¹⁻³⁾.

The bands at 1768 and 1689 cm^{-1} have been assigned to the free and the bonded C=O stretching vibration respectively^{6,7,10)}. However, there remains a problem of the vibrational coupling between the two C=O stretching vibrations. As shown in Fig. 4, the directions of the transition moments do not coincide with the C=O band directions. This can be explained by considering that the band at 1768 cm^{-1} is mainly due to the free C=O stretching and slightly to the bond-

ed C=O stretching (in phase), and that the band 1689 cm^{-1} is due to the bonded C=O stretching and free C=O stretching (out-of-phase).

The two bands at 1416 and 1190 cm^{-1} have been assigned to the mixed modes of the C-N-C antisymmetrical stretching and NH in-plane deformation modes respectively¹⁰. It is expected that the directions of the transition moments of these vibrations are perpendicular to the NH bond direction. As shown in Fig. 4, the directions of the transition moments agrees satisfactorily with the expected direction. The band near 850 cm^{-1} has been assigned to the NH out-of-plane deformation, and has been regarded as the overlapping of two bands¹⁰. Polarized infrared spectra show that the band consists of two bands at 841 and 850 cm^{-1} . For the band at 850 cm^{-1} the absorption is strong when the radiation is polarized with the E vector parallel to the b axis, and weak when the E vector is parallel to the a and c crystal axis. The D_c^a of the band at 841 cm^{-1} may be measured quantitatively, but D_c^b of this band can not, because of the overlapping with a band at 850 cm^{-1} . However, the intensity of the absorption parallel to c axis is stronger than that parallel to b axis. This means that θ_c^b have a value lower than 45° . Referring to Fig. 2, the absorption band at 841 cm^{-1} can be assigned to NH out-of-plane deformation mode.

The band near 640 cm^{-1} has been assigned to C=O in-plane deformation mode. The polarized infrared spectra show that this band is overlapped by two bands at 650 and 640 cm^{-1} . By referring to the values of θ_F^x , the bands at 650 and 640 cm^{-1} are assigned to the antisymmetric and symmetric C=O in-plane deformation vibrations respectively. The band at 558 cm^{-1} has been assigned to the C=O out-of-plane deformation mode¹⁰.¹ Although this band could not quantitatively be treated because of the absorption of rock-salt plates, it can be assigned to the out-of-plane vibration by its polychroism.

1.2. Bands due to $-\text{CH}_2-\text{CH}_2-$ group. The band at 2960 cm^{-1} is obviously assigned to the CH stretching. The direction of the transition moment of this band could not be measured because of its weak intensity and overlapping with the NH band.

The band at 1429 cm^{-1} has been assigned to the symmetric CH_2 deformation mode¹⁰. The θ_F^x of this band is about 145° , and has an expected direction. By referring to the direction of the transition moment and the frequency, the band at 1397 cm^{-1} is assigned to the CH_2 antisymmetric deformation mode. The band at 1290 cm^{-1} has been assigned to the CH_2 wagging vibration¹⁰. The θ_F^x of this band is 80° and has an expected direction.

The band at 1242 cm^{-1} has been assigned to the CH_2 twisting vibration. However, the direction of the transition moment shows that the band is an in-plane vibration. If this molecule has a complete C_{2v} symmetry, CH_2 twisting vibrations consist of infrared active (B_2) and inactive (A_2) vibrations. Because of the low symmetry of the molecule in crystal and weak intensity of the band due to twisting, it is hardly justified that their assignment¹⁰ is not appropriate.

The bands at 1002 and 821 cm^{-1} have been assigned to the CH_2 rocking and skeletal vibrations respectively¹⁰. The directions of transition moments of these bands show that the former band is the in-plane and the latter is the out-of-

plane vibrations. Therefore, the bands at 1002 and 821 cm^{-1} are adequately assigned to the skeletal and CH_2 rocking vibrations respectively.

The bands at 934 and 850 cm^{-1} have also been assigned to skeletal vibrations¹⁰⁾. By referring to the directions of transition moments, it is appropriate that the band at 934 cm^{-1} is the CH_2 -CO antisymmetric stretching, and one of the bands at 1002 and 850 cm^{-1} is due to the CH_2 -CO symmetric stretching and the other to the CH_2 - CH_2 stretching vibration.

1.3. Molecular interaction. It has been mentioned above that equation (1) can be used only when the coupling between molecules within the unit cell is small. However, the succinimide molecules in crystal have intermolecular hydrogen bonds. Thus, applicability of equation (1) to this molecule is discussed from the factor group analysis.

Succinimide crystallizes in the space group $P_{bca}-D_{2h}^5$ with eight molecules per unit cell¹²⁾. In the crystal, a dimer is formed by the hydrogen bond, with the site symmetry C_i in the center. In accordance with the results of the factor group analysis (Table 3), each of the 30 fundamental molecular vibrations is splitted to eight species. Here four (A_g , B_{1g} , B_{2g} and B_{3g}) are active only in the Raman spectrum, one (A_u) is inactive in the Raman and infrared spectra, and the remaining three (B_{1u} , B_{2u} and B_{3u}) are active only in the infrared spectrum.

Table 3. Factor group analysis of succinimide.

D_{2h}^{15}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	N	T	T'	R'	n	IR
A_g	1	1	1	1	1	1	1	1	36	0	3	3	30	
B_{1g}	1	1	-1	-1	1	1	-1	-1	36	0	3	3	30	
B_{2g}	1	-1	1	-1	1	-1	1	-1	36	0	3	3	30	
B_{3g}	1	-1	-1	1	1	-1	-1	1	36	0	3	3	30	
A_u	1	1	1	1	-1	-1	-1	-1	36	0	3	3	30	
B_{1u}	1	1	-1	-1	-1	-1	1	1	36	1	2	3	30	M_z
B_{2u}	1	-1	1	-1	-1	1	-1	1	36	1	2	3	30	M_y
B_{3u}	1	-1	-1	1	-1	1	1	-1	36	1	2	3	30	M_x

N : number of oscillations under each species.

T : number of translations under each species.

T' : number of translatory types of external oscillations under each species.

R' : number of rotatory types of external oscillations under each species.

n : number of the internal oscillations under each species.

All vibrations belonging to the infrared active species are antisymmetric to the center of symmetry. The three infrared active species are produced by phase differences of the same mode of four dimers. Therefore, applicability of equation (1) depends on the interaction between dimers, but not on hydrogen bonds in dimers.

From the results of X-ray analysis¹²⁾, the imide group has an approximate symmetry plane. Therefore, when interaction between dimers is small, all vibrations of the imide group should be in the expected positions; that is on the closed curve for in-plane and a position marked X for out-of-plane vibrations as shown in Fig. 2. In fact the bands assigned to the vibrations of the imide group

are in expected positions. This indicates that the interaction between dimers is small. The deviation from the curve for the bands assigned to vibrations of $-\text{CH}_2-\text{CH}_2-$ group can be interpreted by the incorrectness of the C_s symmetry in the group¹²⁾ rather than by the interaction between dimers from the above discussion and the previous results⁴⁾.

2. Acetanilide

Figs. 7(a) and (b) show the polarized infrared spectra of the two samples, in which (100) and (010) crystal faces are parallel to the surface of rock-salt. The spectra and the present dichroic ratios match to those reported by Abbott *et al*¹¹⁾. Table 7 shows dichroic ratios, as well as θ_b^a and θ_c^b calculated by equation (1). When θ_b^a and θ_c^b are plotted in Figs. 5 and 6, observed values are found either close to one of the two curves or one of the two positions marked X. It appears that the mixing of vibrations of the amide and benzoic groups is small. The above method may be applied to the molecules with two symmetry planes. Occasionally, the two curves cross one another, for example, when θ_b^a is 56° and θ_c^b is 73° . It is very difficult to distinguish whether the absorption is derived from the amide or benzoic group. They are the bands

Table 4. Atomic coordinates of amide group (A unit).

	$X(A)$	$Y(A)$	$Z(A)$
C ₁	8.73	-0.36	-0.17
N	10.08	0.07	-0.05
C ₇	11.20	-0.66	-0.02
C ₈	12.49	0.06	-0.05
O	11.17	-1.88	-0.05
H ₁	10.11	1.15	-0.07
H ₇	13.35	0.01	-0.85
H ₈	12.71	-0.55	0.69
H ₉	12.42	1.05	0.15

Table 5. Atomic coordinates of benzoic group (A unit).

Atom	$X(B)$	$Y(B)$	$Z(B)$
C ₁	8.17	-0.02	-0.02
C ₂	7.17	0.90	0.01
C ₃	5.82	0.46	0.00
C ₄	5.54	-0.88	0.00
C ₅	6.59	-1.81	-0.01
C ₆	7.91	-1.38	0.02
N ₁	9.50	0.51	-0.02
H ₁	9.46	1.55	0.25
H ₂	7.38	1.94	0.02
H ₃	5.01	1.15	0.02
H ₄	4.53	-1.21	0.01
H ₅	6.37	-2.84	-0.02
H ₆	8.71	-2.06	-0.00

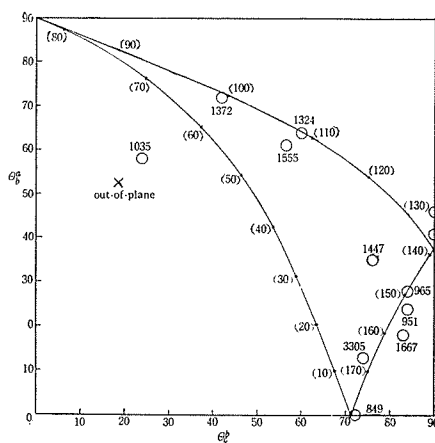


Fig. 5. $\theta_b^a - \theta_c^b$ plotting of amide group.

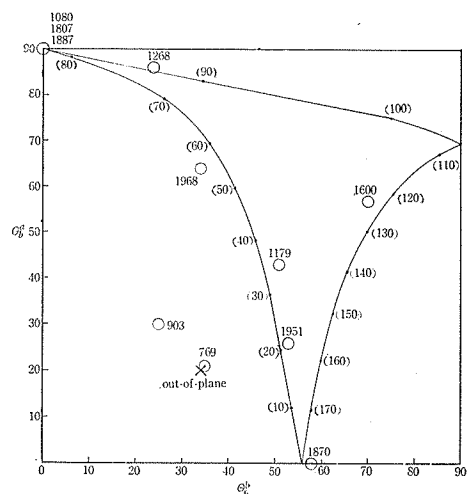


Fig. 6. $\theta_b^a - \theta_c^b$ plotting of benzoic group.

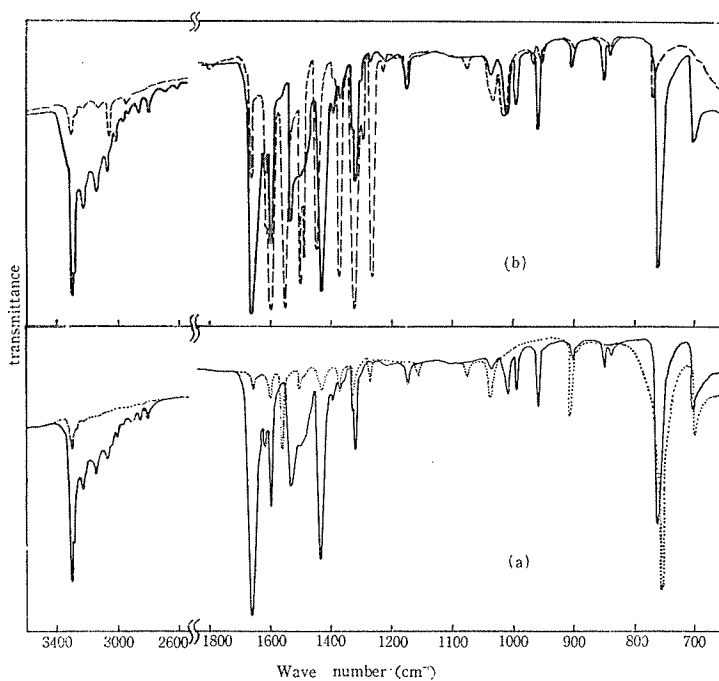


Fig. 7. Polarized infrared spectra of acetanilide.

a : 100 section. *b* : 001 section.

----- *E* vector along *a* axis.

— *E* vector along *b* axis.

..... *E* vector along *c* axis.

at 1179, 1600, 1951 and 1968 cm^{-1} . In such cases, it is necessary to determine the direction of the transition moment from dichroic ratios and the assignment employing another method.

2.1. *N*-deuterated compound. Acetanilide crystallizes in the space group $P_{bca}-D_{2h}^{15}$ with eight molecules per unit cell⁽¹¹⁾. Each of 51 fundamental molecular vibrations was splitted to eight species. It is necessary to apply the product rule for one species. In the infrared spectra, E vector is parallel to one of the three crystal axes. Table 6 shows the result of the application of product rule to acetanilide and *N*-duterated compound. Here E vector is parallel to the b crystal axis except the band assigned to CH_3 asymmetric deformation vibration. When E vector is parallel to b axis, this vibration shows no absorption and thus the frequency is given with the E vector parallel to c axis. An experimental value in Table 6 gives a ratio of 1.90 for the in-plane vibration of the amide group. When the molecule is not planar, its theoretical ratio can not be accurately calculated. A value slightly below two obtained in this determination may be considered reasonable from the size of this molecule.

Table 6. Frequency changes on deuteration.

Assignments	Undeuterated compounds	Deuterated compounds	Frequency ratios
NH, ND	3294	2420	1.36
Amide I, I'	1666	1640	1.02
Amide II, II'	1538	1402	1.10
CH_3 Asymmetric deformation	1436	1485	0.97
Amide III, III'	1322	980	1.35
$\text{C}_1\text{-N}$	1267	1312	0.97
$\text{CH}_3\text{-C}$	1012	1068	0.95
CH_3 in-plane rocking	960	935	1.03

2.2. Characteristic bands due to the amide group. The $\theta_F^X(A)$ of a band due to NH stretching vibration is 167° as shown in Table 7. This direction gives an angle of about 14° for the NH bond with 1° as $\theta_F^X(A) [X]$. Similar results, in which the direction of the transition moment did not coincide with the NH bond direction for succinimide and other cases, were reported⁽¹⁻³⁾. The angle between the C=O bond and the direction of the transition moment of a band assigned amide I is 22° and this agrees with the result reported by Abbott *et al.*⁽²⁾. The reason for the disagreement may be caused by the transfer of electron rather than coupling of vibration as mentioned by Fraser *et al.*⁽¹³⁾ This interpretation is favored by the fact that the dichroic ratio of the band due to ND stretching or amide I' of *N*-deuterated compound is similar to the corresponding bands of undeuterated sample. The $\theta_F^X(A)$ of the band due to amide II is 180° , as shown in Table 7. This direction agrees with the results⁽¹⁻³⁾ for some amide compounds and with the calculation by Miyazawa *et al.*⁽¹⁴⁾

The assignment of the amide III has not yet been confirmed. One of the bands at 1324 and 1268 cm^{-1} following deuteration may be assigned to this vibration (Table 3). Compared to the frequencies of amide III of other amide compounds, it appears to be appropriate to assign the band at 1268 cm^{-1} . However, dichroic ratios suggest that the band at 1324 cm^{-1} is due to the vibration of

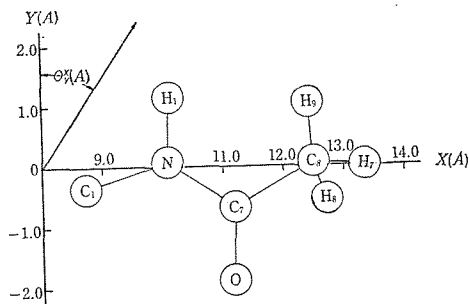


Fig. 8. Projection of amide group to XY plane and directions of transition moments.

Table 7. Frequencies, dichroic ratios, directions of transition moments and assignments of acetanilide.

Frequencies (cm^{-1})			D_a^a	D_c^b	$\theta_b^a(^{\circ})$	$\theta_c^b(^{\circ})$	$\theta_F^x(A)(^{\circ})$	$\theta_F^x(B)(^{\circ})$	Assignments
a	b	c							
3305	3294	3307	0.05	12.45	13	74	167		NH st.
1968	1968	1968	4.20	0.46	64	34		56	Combinations
1951	1951	1951	0.23	1.77	26	53		21	
1887	—	1887	∞	0	90	0		82	
—	1870	1870	0	2.47	0	58		0	
1807	—	1807	∞	0	90	0		82	
1667	1666	1669	0.10	61.99	18	83	159		Amide I
1600	1600	1604	2.33	7.68	57	70		125	Ring st.
1555	1538	1562	3.27	2.14	61	56	108		Amide II
1503	sh.	sh.							Ring st.
1490	sh.	sh.							
1447	1436	1435	0.48	15.71	35	76			CH_3 asym. bend.
1372	1372	1372	9.47	0.79	72	42	100		CH_3 sym. bend.
1324	1322	1327	4.16	3.01	64	60	109		Amide III
1268	1267	1268	182.6	0.20	86	24		88	C_1 N st.
1179	1179	1159	0.93	1.51	43	51		35	CH in-plane bend.
1080	—	1080	∞	0	90	0		82	CH in-plane bend.
1035	1041	1042	2.47	0.21	58	24			CH_3 out-of-plane rock.
1014	1012	—	1.07	∞	46	90	132		
965	997	998	0.29	91.19	28	84	150		
951	960	951	0.20	83.64	24	84	153		CH_3 in-plane rock.
903	905	907	0.33	0.23	30	25			CH out-of-plane bend.
—	849	843	0	9.95	0	72	0		
838	838	—	0.76	∞	41	90	135		
769	761	752	0.14	0.49	21	35			CH out-of-plane bend.

amide group, as shown in Fig. 5, and the band at 1268 cm^{-1} is due to a vibration of benzene group as shown in Fig. 6. The nitrogen atom is not on the plane of amide group but on the plane of benzene group, as shown in Tables 1 and 2. From the above mentioned results, it will be concluded that the bands at 1324 and 1268 cm^{-1} are assigned to the amide III and C_1N stretching vibration respectively. Disappearance of the band on deuteration explains that the band is

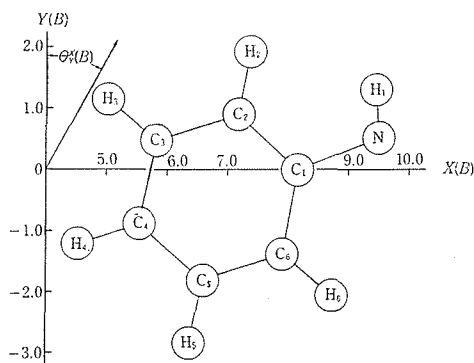


Fig. 9. Projection of benzoic group to XY plane and directions of transition moments.

due to the vibration of the mixed NH bending. The bond distance of C_1N can be estimated to be 1.425\AA from the results of X-ray analysis. Therefore, it seems that the frequency of the band is a reasonable value.

2. 3. Bands due to CH_3 group. The band at about 1440 cm^{-1} can be assigned to the CH_3 asymmetric deformation vibration. This band is not present on the curve in Fig. 5. This is caused by the small splitting of the band to the in-plane and out-of-plane vibrations. The band at 1372 cm^{-1} is assigned to the CH_3 symmetric deformation mode. The θ_F^Y (A) of the band is 100° , and gives an angle of about 20° with the direction of C_7C_8 bond.

The band at 1035 cm^{-1} is assigned to the out-of-plane vibration of the amide group from Fig. 5. It is appropriate to assign this band to the CH_3 out-of-plane rocking vibration. The band at 965 or 951 cm^{-1} may be due to CH_3 in-plane rocking vibration. The disappearance of the band at 951 cm^{-1} on deuteration indicates that the band should be assigned to CH_3 in-plane rocking vibration.

2. 4. Benzene ring. The direction of transition moments of hydrogen out-of-plane vibrations and their combination bands have been reported previously⁴¹. With the present method, these directions is determined easily without any tedious calculation and the results are shown in Table 7.

Other vibrations of benzene ring are hydrogen in-plane deformation and skeletal vibrations. The band at 1600 cm^{-1} may be assigned to the CC stretching vibration. Assuming that the symmetry of benzene ring is C_{2v} , CC stretching vibrations can be divided into A_1 and B_1 species. However, the direction of the transition moment of the band does not coincide with either direction correspond to the both species. As the band is on the curve of Fig. 6, the benzene ring is considered to have the C_s symmetry. This result agrees with the conclusion obtained previously⁴¹.

The bands at 1179 and 1080 cm^{-1} are assigned to the CH in-plane deformation vibration. The directions of transition moments of the bands also indicate that the C_s rather than C_{2v} symmetry is more appropriate.

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